Current Transients in CdS/CdTe Solar Cells

Alan Fahrenbruch
Colorado State University
Department of Physics
Fort Collins, CO 80523-1875

ABSTRACT

Current transient responses to voltage and illumination steps are investigated to clarify the mechanisms involved in carrier transport in CdS/CdTe cells. For most cells, the response to a dark, forward-bias step after a long dark soak at zero bias is a current growth curve For one such cell, the magnitude of the transient is ≈ 22% of the starting value with half of the growth occurring within ≈ 5 sec, the other half requiring 1000's of seconds. The effect is completely reversible and a mirror-image decay curve at zero bias after dark bias-on equilibration can be measured. Similarly, a complex of growth and decay curves are observed on application of illumination steps with constant bias. Similar transients have been observed by McMahon [1] and del Cueto et al. [2]. This is a survey of these effects in cells from three different fabricators.

These transients, with varying magnitudes and directions, were seen in all the cells studied. In general, the better the cell, the smaller the magnitudes of the transients. They range from changes by factors of 10 for pathological cells to subtle transients of 1-2% in excellent cells.

Beside the important implications these transients have for accurate measurements of cell efficiency and stability, they provide clues about the carrier transport mechanisms.. One of the mechanisms proposed involves the occupation of deep donor traps with small hole cross sections, changing their recombination kinetics. The second hypothesis involves the modulation of the junction barrier profile by changing the charge on deep acceptors and donors by carrier trapping, leading to a change in the effective junction barrier height. A third involves defect mutation such as that of [Cu_i] donors into [V_{Cd}- Cu] acceptor complexes, depending on the position of the quasi-Fermi levels.

INTRODUCTION

Although measurement of transients is straight-forward, attributing them to a mechanism and location in the cell is not. Many time constants apply to an electrical or light step response:

MECHANISM	TIME CONSTANT (sec)
Carrier thermalization within bands	10^{-13}
Recombination lifetime	10^{-10} to 10^{-8}
RC time constant for 1 cm^2 cell and 10 Ω	10^{-7} to 10^{-6}
C-V response for shallow states ≈ 1 MHz	10^{-6}
C-V response for deeper states ≈100 Hz to 30 kHz	3 x 10^{-5} to 10^{-2}
Trapping and detrapping times	10^{-4} to 10^{5}

When bias (or light) is suddenly applied to a device, the initial dark current (or light-generated current, J_L) change will occur in times on the order of the recombination lifetime or the RC time constant. Then the occupancies of the conduction and valence bands and the gap and interface states readjust themselves by mechanisms like carrier trapping and defect state mutation toward some steady state. The readjustment can cause changes in the cell current by changing the band profile and/or the recombination losses. This survey focused on currents in the trapping time region.

EXPERIMENTAL DETAILS

Dark current growth transients were measured by sudden application of a forward-bias step (e.g., 0.65 V), after a dark, zero-bias equilibration period of 0.5 to 10 hours at RT called here the "dark soaked" or "DS" state. In most cases continued application of forward bias increases the current asymptotically toward a "forward-bias-soaked" or "FBS" state. The effect is completely reversible, with a decay to the DS state. The current/time data were taken using an HP 7090A

A/D buffer input recorder with a 30 k/sec sampling rate (rise times < 0.01 sec could be measured reliably). J-V data was recorded point by point, holding the bias constant with dwell times of 3 to 10 sec at each bias, using a red (630 nm) LED with an output equivalent to ≈ 1 sun for light data.

Red (630 nm) and blue (470 nm) LEDs were used for light transient measurements, usually with an equivalent photon current density J_{ph} of ≈ 1.4 mA/cm^2. About 80% of the blue was absorbed by the CdS, with low quantum efficiency QE, so that $J_{sc} \approx 0.3$ mA/cm^2. All of the red was absorbed only by the CdTe close to the junction, so its QE was larger, $J_{sc} \approx 1.2$ mA/cm^2.

RESULTS

J-V Characteristics – CSU Cells

The J-V characteristics of the cells varied a great deal between fabricators and treatments. However, the CSU (Sampath) unstressed and stressed cells were very much the same. Both CSU cells showed a gradual irreversible increase in the lower portion of the log J-V curves Fig. 1a, which didn't affect their ff or V_{oc}. Both these cells were exceptional in that there was almost no cross-over. These data (Fig. 1b) suggest that the forward-bias transport is not altered appreciably by illumination; the light curve appears to be simply a dark curve displaced downward by the bias dependent light-generated current density $J_L(V)$ (which might be called quasi-superposition).

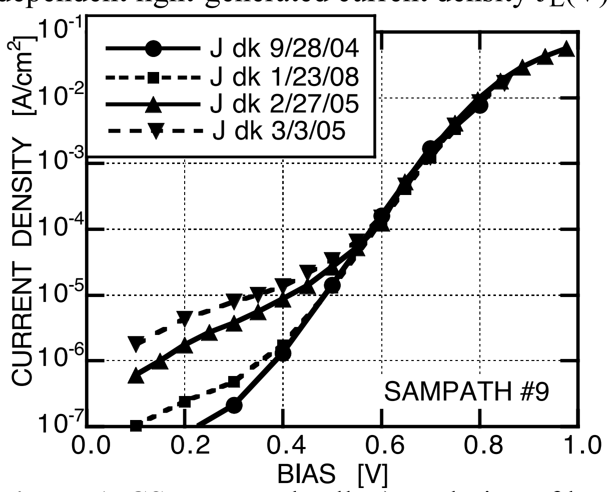

Figure 1. CSU stressed cell: a) evolution of log J-V over time, b) linear J-V showing $J_L(V)$.

J-V Characteristics – IEC Cells

One of the IEC cells had Cr contacts without Cu and the other had Cu-Cr contacts and showed very different behavior (Fig. 2 a and b). The extreme roll-over for the no-Cu cell suggests a high back contact barrier height ($Ø_{bc}$) and low effective acceptor density ($N_a - N_d$) where N_a and N_d are the shallow acceptor and donor densities.

J-V Characteristics –NREL Cells

The NREL cells were processed with less-than-, equal-to-, and more-than-optimum Cu, but otherwise identically. The Cu < opt cell suffered from poor collection and ≈ – 2 V reverse bias was required to pull out the appropriate J_L (Fig. 3 a and b). This suggests that ($N_a - N_d$) < 0, for at least the front part of the CdTe layer, and that the front portion of the bands in the CdTe layer are bent concave upward. The Cu>opt cell had the kind of +, –, + curvature seen in the AMPS [3] modeling of an n-CdS/i-CdTe/p-CdTe/i-CdTe junction with a large $Ø_{bc}$.

Dark Forward Bias Transients

For most of the cells, the transient current response ($\Delta J(V_f)$), following a constant dark, forward-bias step (ΔV_f) and after a long dark soak at zero bias (DS), is a <u>growth</u> curve. The initial, instantaneous step as the bias is turned on (< 0.01 sec) is <u>not</u> included in $\Delta J(V_f)$. For example (Fig. 4a), the magnitude of the transient is ≈ + 22% of the starting value. The effect is completely reversible and a mirror-image <u>decay</u> curve at zero bias after dark bias-on equilibration can be measured using short (≈ 0.2 sec) pulses of V_f as a probe.

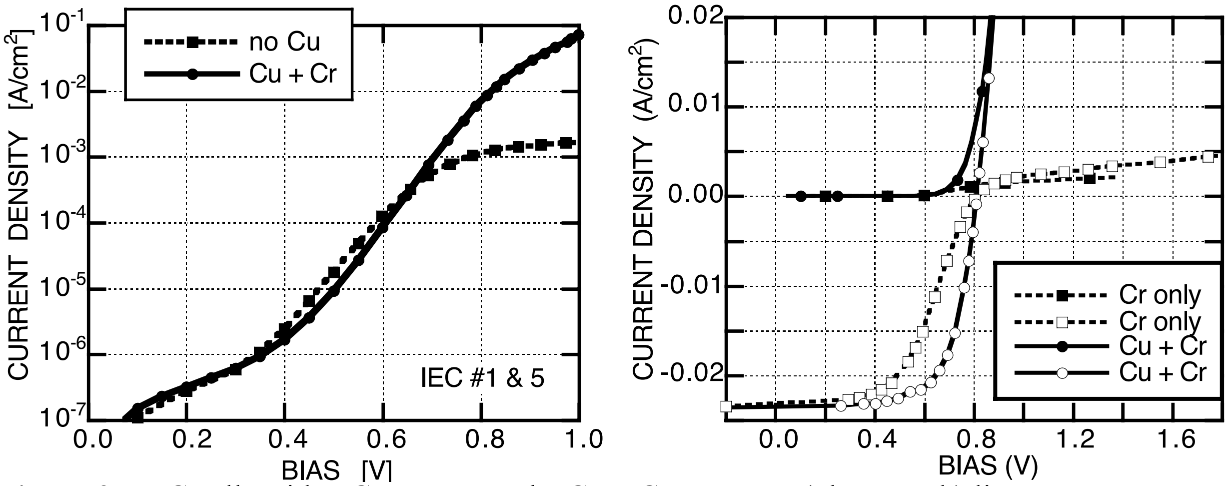

Figure 2. IEC cells with a Cr contact and a Cu + Cr contact: a) log J-V, b) linear J-V.

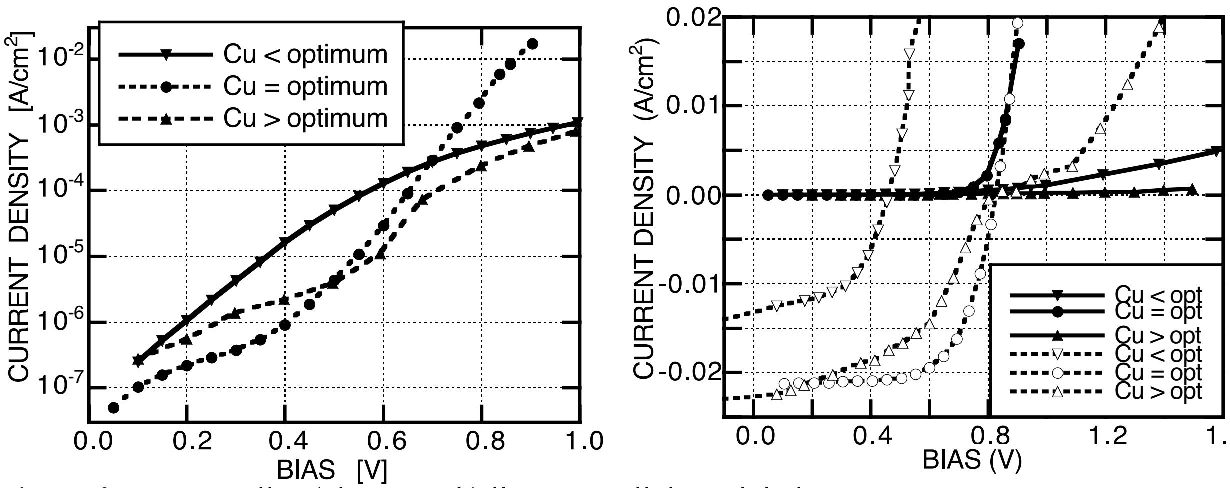

Figure 3. NREL cells: a) log J-V, b) linear J-V, light and dark.

All of the cells have similar transients, but with different magnitudes and directions of growth or decay. A summary is given in Table 1. The ratio of $\Delta J(V_f)$ to the initial J appears to reach a maximum at V_f = 0.6 to 0.7 V. For all the cells, the decay/growth data could be reasonably fit by (a) a sum of exponential growths with time constants ranging from 0.1 to > 400 sec, (b) a stretched exponential, suggesting a distribution of trapping energies, or (c) log(t) for growth and log(1/t) for decay (for most of the central part of the time span).

Similar growth and decay curves are observed with weak illumination before or during the ΔV_f step. In one case, the NREL Cu<opt. cell, red light reversed the decay to a growth. However, at V = 0, on application of red and/or blue illumination pulses, all the cells produce flat bottomed square pulses with no discernable decay or growth of J_{sc}, i.e., $\Delta J(V_f) = 0$ (except Cu < opt, which had a slight decay with red light)..

Light Forward-Bias Transients

For cells at forward bias, the transients resulting from blue or red light pulses were quite varied, ranging from nearly flat ($\Delta J(V_f) \approx 0$) for the optimally processed cells to growth or decay curves with magnitudes and signs depending on V_f. for the imperfect cells. An example of the latter case is the IEC Cr-only cell (Fig. 4b). When blue or red illumination is turned off, the dark current is increased temporarily, but decays rather quickly to a steady dark value. This decay is much faster and closer to exponential than the dark $\Delta J(V_f)$ of Fig. 4a. Another example is the NREL Cu< opt. cell, for which the forward bias current is increased by a factor of 10 by application of red light. (Fig. 5a), followed by a growth which is mirrored by the dark current

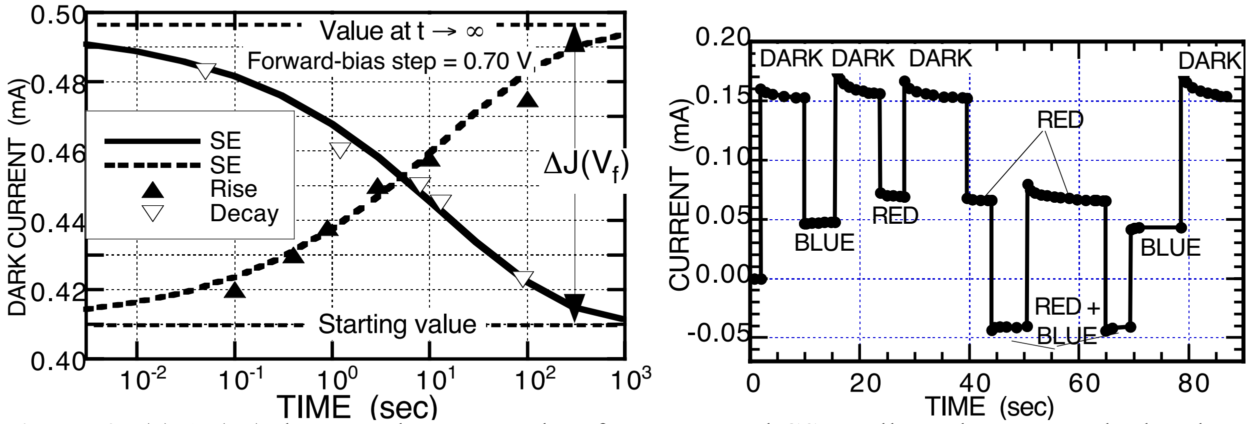

Figure 4. (a) $\Delta J(V_f)$ decay and recovery data for unstressed CSU cell. Both curves calculated using the same stretched exponential parameters: time constant = 15 sec and stretch parameter = 0.35. The stressed cell data are quite similar. (b) Light transients for the IEC Cr-only cell at 0.7 V.

Table 1. Properties of various cells

CELL	CONDI-TION	DARK $\Delta J(V_f)$	LIGHT $\Delta J(V_f)$	RED $\Delta J(V_f)$	BLUE $\Delta J(V_f)$	COMMENT
CSU 15244-1	unstressed	+ 22% R	+ 20-30% R	flat reduction by $J_L(V)$, no transient	reduction by $J_L(V)$, $\Delta J(V_f) = 0$	
CSU 15244-9	stressed	+ 50% R	+ 50% R	flat reduction by $J_L(V)$, no transient	reduction by $J_L(V)$, $\Delta J(V_f) = 0$	
IEC VT128-4	Cr only	– 50% R	≈ – 50% R	flat reduction by $J_L(V)$, no transient	reduction by $J_L(V)$, $\Delta J(V_f) = 0$	
IEC VT128-3	Cu + Cr	± 3% R	≈ + 20% R	flat reduction by $J_L(V)$, no transient	reduction by $J_L(V)$, small transient	prior blue light increased dark $\Delta J(V_f)$ to 20% NR
NREL 699B-4	Cu < optimum	– 25% R	+ 25% w. red R	13 x growth & ramp up R	10 x growth & slow ramp up R	prior red light reversed dark $\Delta J(V_f)$ to + 25% R
NREL 694B-4	Cu = optimum	+ 3% R	+6% w. blue R	flat reduction by $J_L(V)$, no transient	reduction by $J_L(V)$, $\Delta J(V_f) = 0$	prior blue light increased dark $\Delta J(V_f)$ to 6% R
NREL 695B-3	Cu > optimum	± 50% R	≈ + 2200% w. blue R	260% step & complex wave-form	860% step & complex wave-form	$\Delta J(V_f)$ + for Vf < 0.65, – for Vf > 0.65. Very photosensitive

$\Delta J(V_f) = 100*(J_{max} – J_{min})/J_{start}$, where $J_{start} = J_{min}$ for growth and $J_{start} = J_{max}$ for decay. Positive is growth when bias is turned on, negative is decay. R = reversible, NR = not reversible

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decay when the illumination ceases. For the NREL Cu>opt. cell, the light-pulse transients and their decays are superimposed on the slower dark $\Delta J(V_f)$ decay which resumes from where it left off before the light pulses (Fig. 5b). In general, the dark decay and growth and the light transients appear to be separate processes with considerably faster rates for the light transients.

Infrared Quenching

The literature indicates that photoconductivity in the CdS layer, known to have high concentrations of Cu, influences the carrier transport. One of the common signatures of CdS:Cu photo-conductors is infrared quenching in two principal bands: 720 - 1000 nm and 1300 - 1660 nm. Exposure to ≤ 510 nm light enhances the photoconductivity of previously quenched samples. The cells were exposed to combinations of red, blue, and/or ir (940 nm at ≈ 4 mW/cm^2) sources and $\Delta J(V_f)$ was measured at V = 0 and V near V_{oc}. No indication of quenching by the ir was observed for any of the cells, except for NREL Cu < opt. which showed a +10 µA increase in current at V_f = 0.6 V, rather than its normal I_{sc} = – 3 µA (due to the tail of the LED spectral distribution).

However, $J(V_f)$ for several of cells showed blue light enhancement (e.g., Fig. 5b and 6a & b).

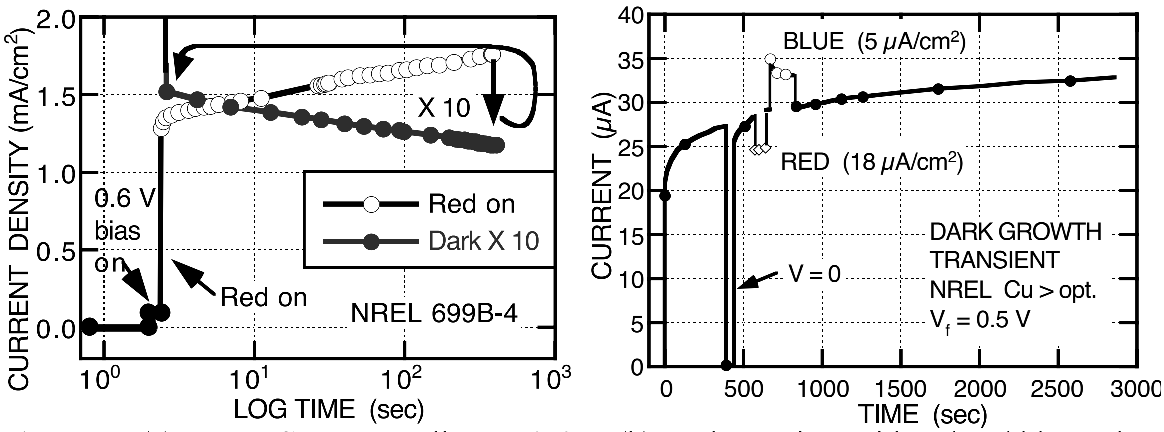

Figure 5. (a) NREL Cu < opt. cell. $V_f = 0.6$ V. (b) Dark transient with red and blue pulses.

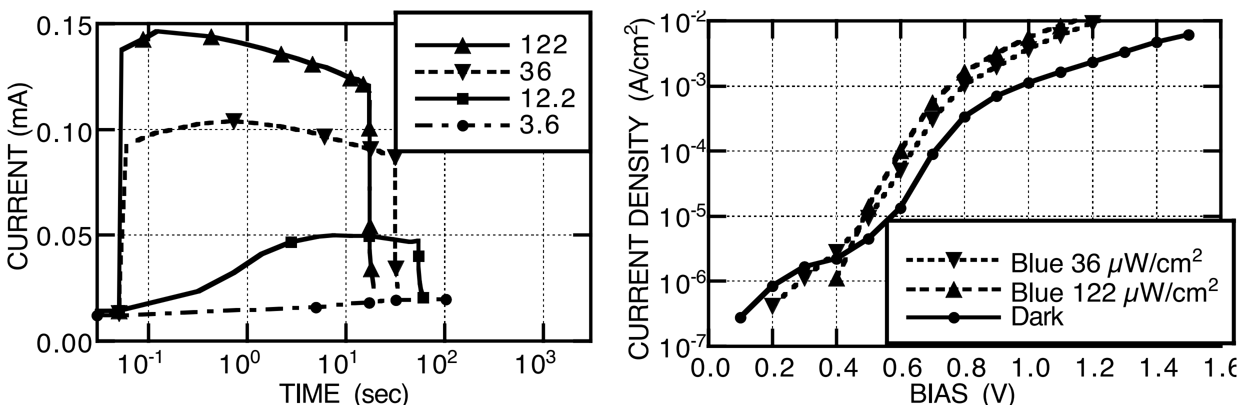

Figure 6. NREL Cu > opt. Blue incident power is in μW/cm^2: a) transients, b) log J-V data

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DISCUSSION

Since all the transients observed occur at currents in the linear region of the log J-V curves (except for NREL Cu < opt.), well below the part influenced by "series resistance" effects, they appear to be properties of the main junction. This is supported by the apparent J_o change for the "dark" log J-V data for the NREL Cu > opt. cell, Fig. 6b, taken with weak bias light.

It appears that the application of bias in the dark moves the quasi-Fermi levels (E_{fn}, E_{fp}) through a density of trapping states in the CdTe, and, for the growth transient, holes are trapped at deep acceptors, making the material more n-type and moving the bands down (Fig. 7). This decreases the barrier for the forward-bias electron current and increases J. Since the movement of the E_{fp} with respect to the trap levels is largest near the CdS/CdTe interface, especially for larger ($N_d - N_a$), it seems more likely that the relevant hole traps would be there and that the growth would be larger for smaller ($N_d - N_a$). Electron traps would be relevant for the decay situation.

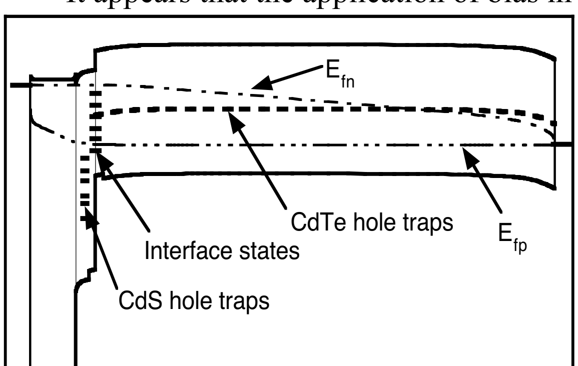

Fig. 7. AMPS simulation of CdS/CdTe cell at 0.7 V forward bias.

In several cases, the dark current is increased above its dark equilibrium value by prior illumination pulses. It then decays over a period of 5 to 10 sec to its dark steady state value when the light is turned off. The currents are small enough so that cell heating is not an issue. AMPS [3] modeling shows that the principal difference between blue and red illumination is that the hole density in the CdS and at the CdS/CdTe interface increases by many orders of magnitude with blue light; while the carrier densities elsewhere are virtually the same. This suggests that the conduction band (CB) in the CdS and/or at the CdS/CdTe interface is moved up and down by carrier trapping there, changing the junction transport.

The NREL Cu = opt. cell responded to light with flat bottomed pulses, with J simply being reduced by $J_L(V)$. However, the blue pulse response for NREL Cu>opt. in Fig. 6a shows a large photoconductivity gain with weak blue light and the response to blue is ≈ 5 times that to red. This points to a photo-gating effect. When the blue light generates a high density of both electrons and holes in the CdS, and when the holes are trapped in the CdS or at the interface, it becomes more n-type and reduces the junction barrier. The notion of trapping is supported by the complex transients seen in Fig. 6a, where several competing mechanisms are evident. The barrier reduction enhances electron transport from the CdS into the CdTe and the current increases substantially. A similar mechanism is found for the "red kink" effect in CIGS cells by Pudov et al. [4].

The red light generates carriers only in the CdTe, and because the CdS VB is a large barrier to holes, mainly electrons are injected into the CdS, and it is more difficult for holes to reach the interface. This may explain the fact that the blue response is much greater than the red and would suggest that the location of the hole traps is at the interface, rather than in the CdS.

CONCLUSIONS

All the cells showed dark forward bias transients, but their magnitude and direction depends on cell preparation. In every case, the transients are reversible and the transient and its recovery can be fit approximately by stretched exponentials.

Bias and light induced transients are small for cells which are well behaved, without roll-over and cross-over and the effect of the transients on efficiency is small.

Cells with pronounced roll-over and cross-over show larger transients. Because (a) in most cases the entire log J-V curve is affected, and (b) bias voltages were chosen in the linear portion of the log J-V curve, the data indicates that the transients are a property of the main junction rather than "series resistance" effects.

The roll-over and cross-over cells also show large, short term (seconds) transients in response to blue (470 nm) and red (630 nm) light pulses, which appear to result from trapping in the CdS layer and/or the CdS/CdTe interface.

None of the cells show the infrared quenching typical of CdS:Cu photoconductors. However, the roll-over and cross-over cells do show enhancement of forward-bias current under blue light, which is also typical of CdS:Cu.

Mechanisms involving trapping of holes and/or electrons in the bulk of the CdTe, the CdS/CdTe interface, and/or the CdS layer have been postulated. The location and type of trapping, are specific to each of the cells.

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